An optical spectroscopic study on two-dimensional group-VI transition metal dichalcogenides

Hualing Zeng and Xiaodong Cui

The ultimate goal of making atomically thin electronic devices stimulates intensive research on layered materials, in particular the group-VI transition metal dichalcogenides (TMDs). Atomically thin group-VI TMD crystals with a 2H stacking order emerging as a family of intrinsic 2-dimensional (2D) semiconductors with a sizeable bandgap in the visible and near infrared range satisfy numerous requirements for ultimate electronics and optoelectronics. In addition, the characteristic inversion symmetry breaking presented in monolayer TMDs leads to non-zero but contrasting Berry curvatures and orbit magnetic moments at K/K' valleys located at the corners of the first Brillouin zone. These features provide an opportunity to manipulate electrons' additional internal degrees of freedom, namely the valley degree of freedom, making monolayer TMDs a promising candidate for the conceptual valleytronics. Besides, the strong spin–orbit interactions and the subsequent spin–valley coupling demonstrated in atomically thin group-VI TMDs open up potential routes towards quantum manipulation. In this tutorial review, we highlight recent advances in the optical study on electronic structures, vibrational properties, excitonic effects, valley dependent optical selection rules, and the interplay of valley, spin, and layer degrees of freedoms in this class of atomic 2D semiconductors including MoS₂, MoSe₂, WSe₂, and WS₂.

Key learning points
(1) An overview of recent significant advances in optical experiments on 2D group-VI TMDs.
(2) Optical properties of monolayer group-VI TMDs as direct band-gap semiconductors.
(3) Optical characterization techniques of 2D TMDs.
(4) Excitonic effects in 2D semiconductors.
(5) Optical study of valley, spin, and layer degrees of freedom in 2D TMDs.

1. Introduction

Novel properties often emerge as the dimensionality of materials is reduced. One example is the behavior of the massless Dirac Fermion displayed in graphene, a truly two-dimensional material with only one layer of carbon atoms that can be exfoliated from bulk graphite.¹,² Pristine graphene is a semi-metal with linear band dispersion in the low-energy electronic structure showing ultra-high ambipolar carrier mobility. However, this gapless character limits graphene's application in electronics as the lack of a bandgap fails to provide an “off” state for a logic transistor which is the building block of modern electronics. The success and the limitation of graphene ignite the research on exploring other 2D atomic crystals, which is not only for the goal of ultimate electronics but also for elegant scientific aspects in the field of physics, chemistry, materials science, and biology. Group-VI transition metal dichalcogenides (TMDs), a class of van der Waals stacked crystals with generalized formula MX₂ (M = Mo, W; X = S, Se), are among the top-notch candidates. The TMDs with a 2H stacking order, which is the most stable phase and the focus of all the interests at this stage, display semiconducting behavior with a suitable energy bandgap in the visible and near infrared range. Analagous to graphite, TMDs can be thinned to ambient-stable monolayers via mechanical exfoliation or chemical synthesis, presenting remarkable physical and chemical properties which are of great potential for applications in optoelectronics, catalysis, sensors, spintronics, and valleytronics.³–¹⁰

The study on the family of MX₂ thin films started as early as in the 1960s, while the focus was only devoted to...
material characterization. Equipped with the pioneering experiences in graphene, Geim’s group first reported the observation of macroscopic monolayer MoS$_2$.\textsuperscript{11} Their semiconducting nature was initially revealed by electrical conductivity measurements, suggesting a sizeable band-gap of energy more than 0.6 eV. Following the fast growing interest in 2D atomic crystals, several years after, two independent groups reported the experimental evidence of the transition from the indirect energy gap at bulk form to the direct band-gap at monolayer MoS$_2$ via photoluminescence (PL) spectroscopy.\textsuperscript{13,14} The next milestone of the 2D TMD research was the demonstration of a monolayer MoS$_2$ field effect transistor with a high current on/off ratio and decent electron mobility more than 200 cm$^2$/V·s at room temperature.\textsuperscript{5} These breakthroughs have greatly stimulated chemists and material scientists to develop new methods to produce ultrathin TMD films in a controllable way, including the chemical vapor deposition (CVD)\textsuperscript{12} and liquid exfoliation.\textsuperscript{13}

Meanwhile, the need for noninvasive and accurate material characterization encouraged the study on vibrational properties\textsuperscript{14–19} and the nonlinear optics.\textsuperscript{15,20–22} Very recently, significant interest rises in attempting to manipulate the spin and valley degrees of freedom in group-VI 2H TMDs owing to the inversion symmetry breaking and the strong spin–orbit coupling (SOC) in monolayer TMDs, i.e. the optical valley control,\textsuperscript{6–9} valley coherence,\textsuperscript{23} and the valley Hall effect.\textsuperscript{24} The strong coupling of the spin and valley degrees of freedom in group-VI 2H TMDs makes them promising candidates for applications in valley based electronics, or so called valleytronics,\textsuperscript{15,25–28} which utilizes the electron’s valley degrees of freedom as an information carrier, analogous to spintronics that exploits electron spin.

Motivated by the rapid progress in the field of layered TMD research, this review focuses on the emerging optical properties of 2H-MX$_2$. For the sake of simplicity, if not specially mentioned, the crystal structure of the group-VI TMD thin films is in the form of the 2H phase. In this review we highlight recent advances in the optical spectroscopic study on this class of emerging 2D semiconductors, mainly on MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$. We review the experimental progress related to the electronic structure, characteristic vibrational modes, structure symmetry and the effect of electron–electron interactions in atomically thin TMD films. We put an emphasis on the unprecedented spin-valley related optical phenomena in both monolayer and multilayer TMDs. In the end, we provide an outlook of the challenges and future developments in 2D TMD research.

2. Fundamental optical properties

The family of group-VI TMDs shares a similar structure of a X–M–X covalently bonded hexagonal quasi-2D network weakly stacked by van der Waals forces usually with a Bernal stacking order (2H). A single layer MX$_2$ (1H) has a prismatic unit cell where the metal atom sits in the center of a trigonal prismatic coordination, being bound to six chalcogen atoms with strong covalent bonds as shown in Fig. 1a. These trigonal prisms are interconnected through the bonds between the chalcogen and metal atoms in the trigonal dipyramidal configuration with $D_{3h}^6$ crystal symmetry. The inversion symmetry is explicitly broken at the single layer since within each slab the chalcogen atoms will be mapped into empty positions if taking the metal atom as an inversion center. Nevertheless, this spatial inversion symmetry is restored in its bulk form as the weakly van der Waals coupled layers follow the 2H stacking order, in which any two adjacent layers are 180 degree in plane rotation of each other (Fig. 1b). The metal atoms of a given layer are sitting exactly on top of the chalcogen atoms of its neighboring layer, which is well represented by the $D_{3h}^6$ space group. The same lattice structure of the materials in the TMD family naturally brings the essentially similar physical properties, including the electronic band structure, the phonon modes, and the structure symmetry.

As van der Waals packed layered materials, ultrathin TMDs can be prepared by mechanical exfoliation from bulk single crystals. This method was initially developed in the discovery of graphene. Tremendous efforts made on the direct large-scale

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middle point between the high symmetric TMDs, the conduction band minimum (CBM) is located at the one at the limit of monolayers. For bulk and multilayer to be metallic. The structure change from the 1T phase to the electronic structures, for example the 1T phase, which is proved to be metallic. The structure change from the 1T phase to the 2H phase can be achieved by low temperature annealing.

Identifying 2D TMDs is readily realized using a regular bright field optical microscope. Monolayer and multilayer TMDs on dielectric capped substrates can be visualized under an optical microscope due to the color contrast, which offers the most efficient way for thickness screening. Quantitative optical characterization on film thickness could be provided with Raman, photoluminescence and second harmonic generation spectroscopy, which all will be addressed in this tutorial. Further characterization can be achieved by various means such as scanning probe microscopy and transmission electron microscopy.

2.1 Electronic properties

Recent theoretical calculations show that the low-energy electronic states are strongly dependent on crystal thickness in atomically thin MX$_2$ films. There exists a crossover from an indirect-gap semiconductor at multilayers to a direct-band-gap one at the limit of monolayers. For bulk and multilayer TMDs, the conduction band minimum (CBM) is located at the middle point between the high symmetric K and $\Gamma$ points in the Brillouin zone, while the valence band maximum (VBM) pins at the $\Gamma$ point, leading to an indirect band-gap. As the bulk thins to monolayers, both the CBM and VBM shift to the $K$ point due to the quantum confinement effect in the 2D system, which yields a direct-gap semiconductor for monolayer TMDs. The intriguing evolution of the electronic band structure presented in ultra-thin MX$_2$ films results from different origins of the electronic states at $K$ and $\Gamma$ points. The conduction and valence bands near $K$ points come from the hybridization of the d-electron orbits of the metal atoms, which are localized and insensitive against interlayer hopping since the metal atoms are located in the middle layer of the X–M–X sandwich. Comparatively, the states near the $\Gamma$ point carry the characteristics of the anti-bonding p-orbits of chalcogen atoms. They are affected strongly by the interlayer coupling and their energies depend sensitively on their thickness. Atomically thin TMD films, including monolayers and multilayers, present an emergent class of 2D semiconductors that can be widely recognized as a platform for ultimate electronics. Especially at the monolayer limit, the sizeable direct band-gap in the visible and near infrared range makes them ideal candidates for optoelectronic applications.

As the electronic properties of the family of group-VI TMDs are similar, herein we take MoS$_2$ and WS$_2$ as typical examples. Fig. 2a and d show the calculated electronic structures of monolayer, bilayer and bulk MoS$_2$ and WS$_2$ by first principles simulations respectively. The band-gaps of both MoS$_2$ and WS$_2$ nanosheets show a dramatic thickness dependence. It shifts from 1.2 eV (1.3 eV) at bulk form to 1.9 eV (2.1 eV) in the monolayer limit for MoS$_2$ (WS$_2$). Accompanying the increase of the band-gap with the decreased layer thickness, they come across a transition from indirect band-gap materials to direct-gap semiconductors as both the CBM and VBM shift to $K$ points at monolayers due to the quantum confinement effect. This change in electronic properties can be monitored by the energy evolution of the absorption/reflection spectra and the band-edge emissions in the PL measurements. Besides, the strong evidence of the direct band-gap at monolayers lies in the PL intensity (quantum efficiency) of monolayers is several orders of magnitude higher than that of the bulk counterparts, as the involvement of phonon- or defect-scatterings for satisfying the momentum conservation in optical transitions is waived in direct-gap semiconductors. The PL quantum yield of monolayers was found to be 10$^4$ fold of that in bulk, which is consistent with the characteristic of a direct-gap semiconductor. Representative observations on MoS$_2$ and WS$_2$ are shown in Fig. 2. This makes monolayer TMDs ideal candidates for optical emitters, photovoltaic cells, and optoelectronic devices.

As ultrathin TMDs are 2D atomic crystals presenting an ultimate surface-to-volume ratio, all chemical bonds are exposed as surface states which are sensitive to environment perturbations. Consequently surface modifications in 2D TMDs play a much more pronounced role in modifying their electronic properties than in their bulk counterparts. Recent experiments clearly demonstrated that the electronic structure and optoelectronic properties of monolayer TMDs can be significantly yet selectively tuned by chemical functionalization with some functional groups. The high sensitivity and reasonable selectivity of the electronic and optoelectronic properties to chemical modifications stimulate growing interest in potential applications of chemical and biological sensing and catalysis.

Another distinct feature of atomically thin TMD films is the giant Zeeman-like spin–orbit coupling (SOC) originating from the heavy metal d-orbits. For monolayer TMDs, both the conduction and valence band edges located at $K$ points are constructed by heavy metal d-orbits $d_{xy}$ and the mix of...
$d_{x^2-y^2}$ and $d_{xy}$ respectively. Band structure calculations show that the SOC splits the valence band into two at the top (K points) while the degeneracy of conduction band remains, which can be seen from the band structure of monolayer MoSe$_2$ as shown in Fig. 3a.\textsuperscript{6,35,36} The magnitudes of the valence band splitting are predicted to be from 160 meV to 460 meV, which equals to the Zeeman splitting strength for electrons in a magnetic field up to $10^3$ and even $10^4$ Tesla. The split valence bands at K points give rise to two direct interband optical transitions, namely the A and B excitonic transitions. By monitoring the energy difference between A and B transitions in optical spectra, for instance the absorption spectrum, the differential transmittance/reflectance measurements, or the PL spectra, the splitting strength can be directly determined as demonstrated in Fig. 3b.\textsuperscript{36} The values of the SOC induced valence band splitting are found to be around 0.15 eV and 0.2 eV for MoS$_2$ and MoSe$_2$ respectively,\textsuperscript{7,4,36} which are greatly enhanced in tungsten dichalcogenides with the value of around 0.4 eV for both.\textsuperscript{15,31} The giant SOC in ultrathin TMD layers benefits them in potential applications in spintronics.

Fig. 3  Optical signatures of spin–orbit coupling in monolayer TMDs (courtesy of ref. 36). (a) Band structure of monolayer MoSe$_2$ calculated by DFT with the correction of SOC. The arrows in red and blue indicate the A and B direct-band-gap excitonic transitions respectively. The valence band at the K point shows a splitting of 180 meV. (b) Low temperature (20 K) differential reflectance spectrum. The sharp peaks labelled A and B correspond to the band-edge excitons originating from spin–valence bands at the K point.
To give a clear summary for the fundamental optical properties of 2D TMDs, we make a table listing the transition energies for the A and B excitons and the SOC strength in all four monolayer TMDs (Table 1).

### Table 1  Summary of the electronic properties of 2D TMDs

<table>
<thead>
<tr>
<th></th>
<th>A (eV)</th>
<th>B (eV)</th>
<th>SOC (2\text{I}) (meV)</th>
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</thead>
<tbody>
<tr>
<td>MoS\textsubscript{2}</td>
<td>1.88 in ref. 3</td>
<td>2.03 in ref. 3</td>
<td>150</td>
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<tr>
<td>MoSe\textsubscript{2}</td>
<td>1.67 in ref. 37 at 20 K</td>
<td>1.87 in ref. 37 at 20 K</td>
<td>200</td>
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<tr>
<td>WS\textsubscript{2}</td>
<td>1.94 in ref. 15</td>
<td>2.33 in ref. 15</td>
<td>390</td>
</tr>
<tr>
<td>WSe\textsubscript{2}</td>
<td>1.65 in ref. 15</td>
<td>2.05 in ref. 15</td>
<td>400</td>
</tr>
</tbody>
</table>

2.2 Vibrational properties

Raman and infrared (IR) spectroscopy are the major techniques to evaluate the vibrational modes. Given the tiny size (usually tens of microns) of the current exfoliated 2D TMD crystals, however, the IR study is rarely reported partially due to the limit of spatial resolution and a low cross section. Raman spectroscopy has been proven to be an accurate and noninvasive technique of thickness characterization as well as a versatile method to study the phonon modes in 2D materials.\textsuperscript{14,16} Intensive research efforts focus on four characteristic Raman-active modes of TMD crystals,\textsuperscript{14–19} namely the A\textsubscript{1g}, E\textsubscript{1g}, E\textsubscript{2g}, and B\textsubscript{2g} modes. These optically active phonons can be divided into two groups as shown in Fig. 4a. A\textsubscript{1g} and E\textsubscript{1g} modes originate from the optical vibrations of the metal and chalcogenide atoms within the same slab, while the latter two modes are from the rigid motion of the whole layer relative to each other. The thickness monitoring technique with the Raman scattering spectroscopy on TMD multilayers was firstly demonstrated by Lee et al.\textsuperscript{14} in MoS\textsubscript{2} thin films, where the energy difference \( \Delta \omega \) of the out-of-plane vibrational A\textsubscript{1g} mode and the in-plane vibrational E\textsubscript{1g} mode was used as a film thickness indicator. For monolayer MoS\textsubscript{2} \( \Delta \omega \) is around 19 cm\textsuperscript{-1} while its value increases to 21 cm\textsuperscript{-1} in bilayer MoS\textsubscript{2}, showing a strong thickness dependence which can be clearly seen in Fig. 4b and c. Similar layer thickness dependence of A\textsubscript{1g} and E\textsubscript{1g} modes in WX\textsubscript{2} has been observed but with much less significance.\textsuperscript{15,19} It is because the heavier tungsten atom makes the eigen-vibrational frequency less sensitive to the environmental changes. Nevertheless, among their Raman active phonon modes the E\textsubscript{2g} and B\textsubscript{2g} vibrational modes are generic for the

Fig. 4  Raman scattering spectroscopy on TMDs. (a) Schematic of four Raman-active modes in 2D TMDs. (b) Raman spectra of thin (few-layer) and bulk MoS\textsubscript{2} films (courtesy of ref. 14). (c) Frequencies of A\textsubscript{1g} and E\textsubscript{1g} Raman modes (left vertical axis) and their difference (right vertical axis) as a function of layer thickness (courtesy of ref. 14). (d) Raman spectra of few-layer MoS\textsubscript{2} in the low-frequency range (courtesy of ref. 16). (e) Thickness dependence of the E\textsubscript{2g} shear mode (upper panel) and the B\textsubscript{2g} LBM or compression mode (lower panel) for few-layer MoS\textsubscript{2}. The blue curve is the fitting with the linear chain model. The red and green curves are produced with least-squares fitting (courtesy of ref. 16).
layered crystal structure and can be regarded as collective interlayer phonon modes. As sketched in the lower panel of Fig. 4a, the E$_{2g}$ mode or the so called shear mode is the rigid oscillation of adjacent layers in the layer plane direction, while the B$_{2g}$ mode or the so called “layer breathing mode (LBM) or compression mode” is the rigidly oscillating motions of layers vertical to the layer plan. It is worth nothing that the B$_{2g}$ mode is Raman inactive for bulk TMDs and turns to Raman active at energy phonons in layered TMDs can be directly detected. 16–19

The two low-frequency Raman modes show contrasting thickness dependencies as illustrated in Fig. 4d and e with multilayer MoS$_2$ as an example. 16 The frequency of shear mode E$_{2g}$ shows a significant increase with the increase of the film thickness. In contrast, the frequency of the layer breathing mode decreases with the increase of film thickness and totally fades in bulks. 16 The observed opposite evolution of the two low-frequency interlayer phonon modes provides a more precise thickness measurement for 2D TMDs, for instance, up to 19 layers for multilayer MoS$_2$. 18 Besides, the study on the shear mode and layer breathing mode gives valuable information on the interlayer interactions and their mechanical properties, for example the interlayer frictional force constant and the shear modulus, which were thought to be done impossibly in an optical way.

2.3 Second harmonic generation in 2D TMD thin sheets

The structure symmetry of materials plays an important role in light-matter interactions. For monolayer and odd-numbered TMD ultrathin films with 2H packing order they are non-centrosymmetric as the inversion symmetry is explicitly broken and are classified as the D$_{3h}$ space group. Nevertheless, the spatial inversion symmetry is restored in even-layer TMD crystals with 2H packing order. To probe the structural inversion symmetry of materials, an elegant tool is the second harmonic generation (SHG) in which the nonlinear optical process combines two input photons to one photon with twice the energy. A simple classical model indicates that the efficiency of SHG is determined by the 2nd order susceptibility $\chi^{(2)}$ of the materials by applying a simple symmetry analysis, it is easy to conclude that $\chi^{(2)}$ must be zero for crystals with inversion symmetry as the spatial reversal transformation $r \rightarrow -r$ makes $P(o,r) = -P(o,-r)$, where the light induced material’s polarization could be described in a classical way as $P(o,r) = \varepsilon_0 \chi^{(2)} E(o,r) E(o,r) + ...$. In contrast, significant SHG implies inversion symmetry breaking. Therefore, SHG can be used as a sensitive probe to the inversion symmetry of materials and the experimental evidence has been demonstrated in atomically thin TMD crystals by independent groups. 15,20–22 The efficiency of SHG from 2D TMDs displays an even-odd oscillation with a

![Fig. 5](image-url)

**Fig. 5** SHG in monolayer and multilayer TMDs. (a)–(d) Courtesy of ref. 15; and (e)–(h): courtesy of ref. 22. (a) Optical image of mechanically exfoliated monolayer and multilayer WS$_2$ on Si/SiO$_2$ substrates. (b) Photoluminescence-mapping image at the direct-gap transition. Only monolayers are visible at present due to much higher PL yield. (c) The corresponding SHG on the same sample. The highest intensity labelled in red arises from monolayers. (d) Relative SHG intensity as a function of the film thickness in WS$_2$. The SHG intensity shows an even–odd oscillation dependence on the film thickness. (e) Optical image of a large area of CVD-grown monolayer MoS$_2$. (f) SHG image of a polycrystalline monolayer MoS$_2$ of the same area. The grains and grain boundaries are clearly revealed by the reduced SHG intensity. (g) The direct crystal orientation image shows the crystal orientations of the irregular-shaped polycrystalline aggregates. (h) Schematics show the flakes I and II are two crystals with opposite orientations, as they have the same contrast in crystal orientation maps but a strongly destructive interference boundary. Crystals II and III show an orientation mismatch of ~12°. The crystal groups (a and b) show two cyclic twin boundaries with 60° and 30°, respectively.
decay envelope as shown in Fig. 5 where monolayer and multi-
layer WS$_2$ are taken as an example.\textsuperscript{15} The strongest SHG comes
from monolayer TMDs and intense SHG is observed on odd-
numbered layers only, as illustrated in Fig. 5c. The dramatic
even–odd oscillation pattern of the SHG from 2D TMDs is the
direct evidence for the variation of structure inversion symmetry
(Fig. 5d), which is in consistence with the presence (absence) of
spatial inversion symmetry in even-layers (odd-layers). The layer
number dependent SHG in ultrathin TMD films provides a fast
and \textit{in situ} layer characterization method and confirms the
Bernal stacking order (2H) in multilayer TMDs.\textsuperscript{15}

Further polarization resolved SHG experiments demonstrate
that the SHG microscopy of monolayer TMDs is able to detect
the atomic edge and grain boundaries and determine the
orientations of 2D crystal domains,\textsuperscript{20–22} which are thought to
be carried out only with the help of the atomic-resolution scanning
probe microscopes or transmission electron micro-
scopes. This amazing ability arises from the monolayer TMDs’
spatial symmetry. For monolayer TMDs, the symmetry is
represented by the $D_{3h}$ space group, resulting in three-fold
rotational symmetry of the crystallographic orientation with
respect to the $c$-axis. When the excitation photon in SHG
experiments is linearly polarized and chosen to be in a normal
incidence configuration ($z$), the responses of the two ortho-
gonal components of second harmonic field from monolayers,
$P_x$ and $P_y$, follow sin $3\theta$ and cos $3\theta$ dependence, respectively,
where $\theta$ is the angle between the orientation of incident
polarization and the zigzag in-plane direction in monolayer
TMDs along which the mirror symmetry holds. The polarization
resolved SHG signal $I_x$ or $I_y$ is thus proportional to sin$^2 3\theta$
or cos$^2 3\theta$, showing a strong dependence on crystal orienta-
tion.\textsuperscript{20,21} The sensitivity of the linearly polarized SHG intensity
with respect to the lattice direction makes it possible to identify
the 2D crystal domains and grain boundaries via an all-optical
way, and the technique has been demonstrated in large
CVD-grown polycrystalline monolayer TMDs as shown in the
lower panel of Fig. 5.\textsuperscript{22}

2.4 Excitonic effects in 2D TMD thin sheets

Bulk TMD crystals display an excitonic feature in their optical
properties owing to the van der Waals layered structure and the
heavy effective mass of valence/conduction bands. The binding
energy of exciton, a kind of quasi-particle composed of tightly
bound electron–hole pairs, ranges from 50 to 80 meV (vs. the
thermal energy 26 meV at room temperature \textasciitilde 300 K) in bulk
TMD crystals. In a single-particle picture, optical absorption
occurs when an electron is excited from the valence band to the
conduction band by absorbing a photon with energy no less
than the electronic band gap, and photoluminescence is just
a reverse process but dominated by the band-edge emission,
an optical transition from the CBM to the VBM. The optical transitions are directly related to the electronic band gap. In an
excitonic picture, attractive Coulomb interactions between
photogenerated electrons and holes bond the electron–hole
pairs to excitons, and consequently reduce the threshold of the
optical interband transition by the binding energy of excitons.

If the binding energy is significant compared with the environ-
mental perturbations (\textit{i.e.} temperature), optical properties
would have pronounced excitonic features. Coulomb interac-
tions are dramatically enhanced in 2D crystals compared with
the conventional semiconductors owing to the spatial confine-
ment and the reduced dielectric screening which is particular
for excitons with in-plane orientation.\textsuperscript{37} A direct consequence
of strong Coulomb interactions is the giant excitonic features
dominating the optical properties. The band-edge emissions
and the pronounced absorption peaks of 2D TMD crystals
(not only monolayers, but also multilayers) are attributed to
excitonic transitions, instead of direct band-to-band transi-
tions. Calculations with various methods of density function
theory (DFT) suggest the exciton binding energy of monolayer
TMDs ranging from 0.6 to 1.1 eV which is a significant fraction
of the corresponding band-gap.

Early experimental evidence for the excitonic nature of the
optical transitions in monolayer TMDs comes from the
observation of the electron-bound excitons, so called trions in
the PL and absorption spectra of monolayer MoS$_2$,\textsuperscript{38} and
MoSe$_2$.\textsuperscript{36} The binding energy of the trions in monolayer TMDs
($\sim$20 meV in MoS$_2$, $\sim$30 meV MoSe$_2$, 35 meV in WS$_2$, and
24–40 meV in WSe$_2$) is about one order of magnitude larger
than that in conventional materials and it makes the trion state
easily visible in PL and absorption spectra even at room
temperature as displayed in Fig. 6. It implies strong Coulomb
interactions and subsequently the giant exciton binding energy
in monolayer TMDs.

Conventionally the exciton binding energy is extracted by
the energy difference between the ground-state exciton and the
onset of the direct band-to-band transition (single particle gap)
in the absorption spectrum. In monolayer TMDs, however, the
strong electron–phonon coupling and the energy overlap with
higher energy bands smear the discrete excitonic states and the
onset of the direct band-to-band transition in the absorption
spectrum. There are two routes towards measuring the exciton
binding energy of monolayer TMDs. One is through optical
absorption spectroscopy at cryogenic temperature at which the
electron–phonon coupling is suppressed. Chernikov \textit{et al.}\textsuperscript{39}
observed series of s-type excited states of band-edge excitons
of monolayer WS$_2$ at 4 K. An exciton binding energy of 0.39 eV
was extracted with a modified 2D hydrogen Rydberg model. The
other approach is through two-photon photoluminescence
excitation spectroscopy (TP-PLE) in which the intensity of the
band-edge exciton emission is monitored as a function of two-
photon absorption, each photon with energy below the band
gap. Two-photon absorption could be described as a third order
nonlinear process involving simultaneous absorption of two
photons and may follow the different optical selection rules
from the linear (one-photon) process. For an intrinsic 2D
system, the two-photon absorption is associated with p-type
excitons while the one-photon (linear) process is with s-type
excitons.\textsuperscript{40} Here s- and p-type are the characteristic labels for
exciton envelop functions describing the exciton states in a
similar way to atomic orbitals. The bright excitons in the one-
photon process, for example the high-energy exciton states, are
usually dark in the two-photon process; whereas direct band-to-band transitions survive in both one-photon and two-photon processes. Consequently the high-energy exciton states around $G$ points which may overlap with the onset of band-to-band transition are inactive in two-photon absorption. As the s-type and p-type excitons have different spatial wavefunctions and lifetimes, besides, they may have different strength of exciton–phonon coupling. So the two processes (one-photon and two-photon) probe complementary information. TP-PLE experiments reveal discrete p-type excited states of band-edge excitons and/or the single particle gap. The exciton binding energy is extracted by the energy difference between the optical gap and the single particle gap. Although there exists quantitative discrepancy among the present experimental findings as listed in Table 2, a strong excitonic feature at monolayer TMDs is the consensus. The strong excitonic effect suggests unprecedented strong exchange interactions and many-body interactions in monolayer TMDs.

### 3. Spin and valley physics in 2D TMDs

#### 3.1 Valley polarization in monolayer TMDs via optical pumping

Most conventional electronic devices utilize the electric charge of electrons to perform functions. Unexhausted efforts have been devoted to explore novel electronic technology that exploits other internal degrees of freedom of electrons in addition to electric charge. One representative example is spintronics in which electron spin acts as information carriers. In addition to spin, there exists valley degree of freedom in TMD crystals owing to their hexagonal lattice structures. TMD crystals with a buckled hexagonal lattice have degenerate but inequivalent $K$ and $K'$ valleys at the corners of the Brillouin zone as shown in Fig. 7a. These $K$ and $K'$ (or $-K$) valleys are separated by a big momentum space, offering low-energy carriers another degree of freedom. The occupation of the different valley ($K$ or $K'$) could be used as a representation of binary-value states. One may manipulate the valley degree of freedom for

### Table 2

Summary of the exciton binding energies of monolayer TMDs

<table>
<thead>
<tr>
<th>Monolayer TMDs</th>
<th>Theory (eV)</th>
<th>Experimental (eV)</th>
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<tbody>
<tr>
<td>MoS$_2$</td>
<td>1.1,1.3,1.03</td>
<td>0.57,0.55</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>0.78,0.94</td>
<td>0.55</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>1.04</td>
<td>0.7,0.55</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>0.90</td>
<td>0.6,0.37</td>
</tr>
</tbody>
</table>

Fig. 6 Electrostatic control of exciton and trion states in 2D TMDs. (a, b) Absorption and photoluminescence spectra of monolayer MoS$_2$ at different back-gate voltages. Both the neutral exciton (A) and trion (A$^-$) features (with the corresponding resonance energies indicated by the dashed lines) can be identified (courtesy of ref. 38). (c) Color contour plot of normalized PL spectra in monolayer MoSe$_2$ under various back-gate bias. Free excitons, electron-bound excitons (negatively charged trions) and hole-bound excitons (positively charged trions) are labeled with X$, X^-$, and X$, respectively (courtesy of ref. 36). (d) Illustration of the gate-dependent trion and exciton quasi-particles and transitions (courtesy of ref. 36).
information operations in a similar way to that in spintronics, which leads to the conceptual “valleytronics”. Owing to
the inversion symmetry breaking, there exist non-zero but contrasting orbital magnetic moments at $K$ and $K'$
valleys in monolayer TMDs.\textsuperscript{6,7} These contrasting orbital magnetic moments at $K$ and $K'$
valleys provide a knob to manipulate the valley degree of
freedom. This quantum manipulation could be realized either
by electric means, for instance, via valley Hall effects\textsuperscript{6,24} which
is analogous to spin Hall effects, or by optical ways.\textsuperscript{7–9} It was
predicted that there are valley dependent interband optical
selection rules at $K/K'$ valleys due to the contrasting orbital
magnetic moments and the requirements of conservation of
angular momentum as well.\textsuperscript{6,7} The optical transitions at $K$
and $K'$ valleys have the contrasting circular helicity, \textit{i.e.}, the right
(left)-handed circularly polarized light corresponds to the optical
transition at the $K(K')$ valley. The valley dependent optical
selection rules provide a protocol to address the valley polarization
in monolayer TMDs.

As a result of the spin–orbit coupling and time reversal
symmetry, the Zeeman like spin splitting at valence band edges
has the opposite sign between $K$ and $K'$ valleys at
monolayer TMDs as illustrated in Fig. 7b. The Kramer doublet,
the spin-up state at the $K$ valley $|K\uparrow\rangle$ and the spin-down state at the
$K'$ valley $|K'\downarrow\rangle$, is separated from the other doublets $|K'\uparrow\rangle$ and
$|K\downarrow\rangle$ by the SOC energy which is around 0.16 eV for molybdenum
dichalcogenides and around 0.4 eV for tungsten dichalcogenides.

This strong SOC and explicit inversion symmetry breaking lock
the spin and valley degrees of freedom in 2D TMDs and this
interplay leads to sophisticated consequences. First, spin and
valley relaxation are greatly suppressed at the valence band edges
as an extra necessity of both spin flip and intervalley scattering
has to be satisfied for holes’ relaxation in monolayer TMDs.
Second, the valley polarization often leads to spin polarization
in monolayer TMDs and \textit{vice versa}.

Valley polarization in monolayer TMDs can be easily
achieved by controlling the polarization of the optical excitation,
which has been demonstrated in polarization resolved photoluminescence measurements.\textsuperscript{7–9,23} The valley dependent
optical selection rules suggest optical circular dichroism in the
PL spectrum. In other words, if the monolayer TMD is excited
with circularly polarized light sources the PL will carry the same
circular polarization with that of the excitation. This circular
dichroism of the PL has been reported in all monolayer TMDs
(MoS$_2$, WS$_2$, WSe$_2$, and MoSe$_2$). The behavior is exhibited in
an example of the polarization sensitive PL spectrum taken on
monolayer WS$_2$ under near resonance conditions at low tempera-
ture, as shown in Fig. 7c. The PL of monolayer WS$_2$ exactly
follows the helicities of the exciting laser source. The universal
definition for the degree of circular polarization

$$P = \frac{I(\sigma^+) - I(\sigma^-)}{I(\sigma^+) + I(\sigma^-)}$$

where $I(\sigma^+)$/$I(\sigma^-)$ is the intensity of the
right/left handed circular component of the PL, could be used

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**Fig. 7** Valley-dependent optical transitions in monolayer TMDs. (a) Schematic drawing of the band structure of monolayer TMDs at the band edges located at the $K$ points (courtesy of ref. 6). (b) Schematic of valley-dependent optical selection rules and the Zeeman-like spin splitting in the valence bands of monolayer TMDs (courtesy of ref. 28). (c) Polarization resolved luminescence spectra of monolayer WS$_2$ with $\sigma^+$ detection (red) and $\sigma^-$ detection (black) under near-resonant $\sigma^+$ excitation (2.088 eV) at 10 K. Peak A is the excitonic transition at band edges of $K(K')$ valleys. Inset presents the degree of the circular polarization at the prominent PL peak (courtesy of ref. 28). (d) The degree of the circular polarization as a function of temperature. The curve (red) is a fit following a Boltzmann distribution where the intervalley scattering by phonons is assumed (courtesy of ref. 28).
to quantitatively evaluate the valley polarization. The degree of circular polarization of the PL on monolayer TMDs is roughly constant around the peak position in the PL spectrum, independent of inhomogeneous broadening. At the early stage of the study on valley polarization in monolayer MoS$_2$, the circular polarization $P$ was found to be with relatively low values,$^7,8$ which were in contrast to the theoretical prediction for the validity of fully valley polarization. The deviation might result from the poor sample quality and the effect of substrates,$^3$ which act as atomic scattering centers. The atomic scattering centers waive the requirements of crystal momentum conservation and dramatically increase the intervalley scattering which is the channel for depolarization. This leads to the significant valley depolarization in monolayer TMDs. Experimental findings show that atomically flat boron nitride (BN) substrates or the improved quality of the crystals could lead to near unity valley polarization in monolayer TMD.$^3,49$ In addition, the valley polarization measured by the steady-state PL gives an estimate on the valley lifetime as the circular polarization $P$ is determined by the relation of the excited state lifetime and the valley relaxation time. If a circularly polarized light pumps the $K$ valley only, the dynamics of the exciton density ($N_K$ and $N_{-K}$ on $K$ and $-K$ valleys) can be described by the following equations:

$$\frac{dN_K}{dt} = \frac{N_K}{\tau} + C$$

where $\tau$ is the exciton life time at both $K$ and $-K$ valleys, $\tau_K^{-1}$ is the $K \leftrightarrow -K$ intervalley scattering rate and $C$ is the exciton generation rate. At the steady-state, $\frac{dN_K}{dt} = \frac{dN_{-K}}{dt} = 0$. The dependence of the degree of PL circular polarization $P$ on the steady-state density of excitons ($N_K$ and $N_{-K}$) can be thus described as $P = \frac{N_K - N_{-K}}{N_K + N_{-K}} = \frac{P_0}{1 + \frac{\tau_{K}}{\tau}}$. Valley life time $\tau_K$ could be then inferred from the measured PL circular polarization. The observed values for valley polarization in monolayer MoS$_2$ by different groups,$^7,9,49$ ranging from 30\% to near unity, indicate that the valley can have a longer life time than that of photo-excited carriers, which is one of the prerequisites for practical device applications.

The validity of the valley degree of freedom in monolayer TMDs can be checked by the well-known Hanle effect.$^8,50$ The need of the verification for valley dependent optical selection rules lies in that in many group III–V semiconductors there exist spin dependent optical selection rules, which enable the spin polarization and result in the circular polarization of PL under circularly polarized excitations. It is therefore necessary to clarify that the observed circularly polarized PL in monolayer TMDs originates from valley-dependent other than spin-dependent optical selection rules. This could be done by applying a transverse magnetic field and monitoring the change of the PL helicity. The rotation symmetry protects the spin pointing along the $c$ axis (out-of-plane) direction. An in-plane magnetic field will cause the spin to precess around the applied field, leading to a significant decrease of the spin component projected in the direction of the $c$ axis. In contrast, the valley index is immune to such a transverse magnetic field as there is no direct coupling between the two. Consequently, the measured PL circular polarization in a transverse magnetic field would be greatly suppressed if it is from spin-dependent instead of valley-dependent selection rules, which can be foreseen in standard Hanle experiments. However, the circular polarization of the PL in monolayer MoS$_2$ found to be strongly robust against the transverse magnetic field.$^8,50$ The constant PL polarization could persist in magnetic fields up to 9T as demonstrated in Fig. 8. The robustness of the PL polarization confirms that the valley polarization is the origin of the circularly polarized PL in monolayer TMDs and it manifests the existence of the valley degree of freedom.

Further proof for valley degree of freedom in TMD monolayers is demonstrated by the electrical tuning of the inversion symmetry in bilayer MoS$_2$. The valley dependent optical selection rules arise from the inversion symmetry breaking in monolayers.$^6$ Nevertheless, in bilayer MoS$_2$, the 2H stacking order restores the inversion symmetry, leading to the invalidation of valley selective optical selection rules. As a result, the PL from the direct interband optical transitions at $K/K'$ valleys in bilayers should be unpolarized, which has been observed in pristine bilayer MoS$_2$.$^6$ However, the crystal inversion symmetry can be broken by an out-of-plane electrical field which could come from either external electric gating or interface charging. The interactions with the substrates including charge transfers...
or photo-doping often break the inversion symmetry to some extent and induce a finite circular dichroism in bilayer MoS₂. The electric gating provides a route for breaking the inversion symmetry in a controlled way and induce a valley contrasting magnetic moments and optical selection rules in bilayers. The first demonstration of electrical control on inversion symmetry has been done by Wu et al. through studying the gate voltage dependence of the PL polarization from bilayer MoS₂ in a field-effect-transistor like device. Very recently the in-plane electric field induced circularly polarized band-edge electroluminescence has been reported in monolayer and multilayer WSe₂. It demonstrates a pure electric way to manipulate the valley degree of freedom.

Another intriguing feature in monolayer TMDs is the possibility of coherently manipulating light–matter interaction via valley coherence. In monolayer TMDs, the state \(|K_i\rangle\) at the \(K\) valley and \(|K'_i\rangle\) at the \(K'\) valley are time-reversal images to each other. The quantum trajectories of hot carrier relaxation via intravalley scatterings are the same for both channels at \(K\) and \(K'\) valleys. This is experimentally demonstrated in monolayer WSe₂ by the linearly polarized PL experiments. The linearly polarized light could be treated as a coherent superposition of right- and left-handed circularly polarized lights. Hot carriers generated by linearly polarized excitation at \(K\) and \(K'\) valleys relax to the band-edge via intravalley scatterings of phonons and Coulomb interactions, which share the same quantum trajectories and keep the same phase difference. So the polarization of the band-edge excitons exactly follows that of the excitation source. The ability of addressing valley coherence raises the possibility of coherent manipulation of quantum states via light-matter interactions in 2D TMDs.

### 3.2 Optical signature of spin–valley coupling in multilayer TMDs

In bilayer TMDs, the inversion symmetry is explicitly restored as a consequence of the Bernal stacking sequence. It is demonstrated by the negligible SHG in bilayer TMDs. However, if the spin–orbit coupling is taken into account, the valley physics can survive even in inversion-symmetric even-layer TMDs. In the 2H packing order, each layer is a \(\pi\) rotation of each other and it switches \(K\) and \(K'\) valleys but leaves the spin unchanged, which results in a sign change for the spin–valley coupling from layer to layer as illustrated in Fig. 9. The spin in the same valley of adjacent layers points to opposite orientation. In MoS₂ the SOC is found to be around 0.16 eV, close to the interlayer hopping energy of around 0.1 eV. And the SOC is not strong enough to suppress the interlayer coupling at \(K/K'\) valleys. This is the reason that the circular dichroism disappears in pristine bilayer MoS₂. One could also tune the inversion symmetry breaking in bilayer MoS₂ with an external out-of-planer electric field. In contrast, the SOC in tungsten dichalcogenides is around 0.4 eV, much larger than the interlayer hopping energy. Consequently, the interlayer coupling at the \(K\) valley is fully suppressed by the SOC in tungsten dichalcogenides. So the valley dependent optical selection rules

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**Fig. 9** Structure and optical selection rules in group-VI bilayer TMDs (courtesy of ref. 25). (a) Coordination structure of bilayer TMDs in Bernal stacking order. (b) Optical selection rules in decoupled monolayers with AB-stacking order. Dashed arrows indicate interlayer hopping. (c) Optical transition selection rules in the \(K\) and \(-K\) valleys of bilayers with interlayer hopping. The transitions denoted by the thick (thin) arrows have strength proportional to \(\cos 2\alpha\) (\(\sin 2\alpha\)). The layer polarization of the Bloch states is schematically illustrated with the rectangular blocks where darker color denotes more occupation.
demonstrated in monolayers extend to bilayer/multilayer tungsten dichalcogenides, though only valid for optical transitions at the $K/K_0$ valley. As spin–valley coupling has the opposite sign between each layer, the circular dichroism corresponds to the real spin polarization in the bilayer. Namely the left (right)-handed circular polarization is associated with optical transitions with $|K_m u_i\rangle$ and $|K_0 m l_i\rangle$ as sketched in Fig. 9c, where $u$ and $l$ denotes the upper and lower layers respectively, indicating the extra layer degree of freedom in bilayers. The interplay of valley, spin and layer degrees of freedom stimulates proposals of quantum manipulation via electric and magnetic means. As the spin–valley coupling is particularly pronounced in atomically thin tungsten dichalcogenides, an optical study on bilayer WS$_2$ and WSe$_2$ is more appealing for valley and spin related physics.

Initial experimental hint on the suppression of interlayer hopping for carriers in $K/K'$ valleys by spin–valley coupling in multilayer WX$_2$ comes from the observation of the constant A–B splitting pattern in the PL spectra. The A and B excitons originate from the Zeeman-like spin splitting in the valence band and the energy difference between A and B excitons reflects the SOC strength. The energy difference of the A and B excitonic transitions in multilayer tungsten dichalcogenides is the same as that in the monolayer with an almost constant value of 0.4 eV (Fig. 10a and b: example of multilayer WS$_2$). The observed constant A–B splitting pattern is evidence of the suppression of interlayer coupling around $K/K'$ valleys, as the interlayer coupling if any inevitably modifies the splitting pattern and splitting strength. The spin and valley indices of carriers in $K/K'$ valleys in multilayer WX$_2$ are locked to specific layers, which can be seen from the density distribution of the wavefunction for states at the $K$ or the $K'$ valley (Fig. 10c). The direct evidence of the coupling of valley, spin, and layer degrees of freedom in 2D TMDs lies in the robust circular dichroism observed in bilayer WS$_2$, as sampled in Fig. 11, where the degree of circular polarization of the PL from bilayer WS$_2$ is significantly higher than that of monolayers. Besides, the bilayer WS$_2$ demonstrated a robust valley coherence even at room temperature.

4. Summary and outlook

Atomically thin TMD crystals feature a family of intrinsic 2D semiconductors well recognized as promising candidates for ultimate electronics and optoelectronics. Vast research efforts...
have revealed strong Coulomb interactions, valley related physics, giant spin–orbit coupling, spin–valley coupling, etc. in the 2D TMDs. These unique properties make 2D TMDs an unprecedented platform for the practice of quantum manipulations, valleytronics and spintronics. Besides, the interplay of light-matter interactions, spin, valley, and layer degrees of freedoms in 2D TMDs particularly in 2D tungsten dichalcogenides, raises numerous inspirations of novel quantum manipulations, charge/magnetism sensing beyond physics.

One of the annoying bottlenecks for aspects in fundamental research and the preliminary study on quantum manipulations lies in the imperfect sample quality. One of the subsequent phenomena is the broad linewidth of the photoluminescence spectra among which the best value, around 5 meV at a temperature of 15 K, comes from exfoliated monolayer MoSe$_2$, in contrast with the narrow linewidth of a fraction of 1 meV in GaAs quantum wells. The broad linewidth reflects a strong inhomogeneous broadening due to tremendous defect/imperfection scatterings. The defects and imperfections blur the intrinsic information and modify the properties usually in a negative way. This is likely to be solved with the progress by chemists and material scientists. Another potentially attracting research direction in 2D TMDs is the material engineering on their crystal structure. At the current stage, most research efforts are devoted to TMDs with a 2H stacking order. For a layered material, it is also possible to have other crystallographic phases, for instance, 1T or 3R. The change of the packing order in 2D multilayer TMDs will bring extraordinary optical and electrical properties, *i.e.* the 3R stacking order will keep the inversion asymmetry in multilayer and bulk TMDs which means that the valley and spin physics can be developed to even bulk samples. This will provide rich research opportunities in various fields.

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